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The extraordinary discrepancy between theory and experiment may be removed in two ways: viz. either by halving the formula, or by assuming that the molecule of the dioxide of ethylene-diethyl-diammonium corresponds to 8 volumes of vapour, in either of which cases the theoretical density becomes 2.31, closely agreeing with the experimental number 2.26.

I shall discuss the vapour-densities of the diammonias somewhat more fully in a future communication; but I cannot refrain from pointing out even now, that, by dividing the formula by 2, we arrive at an expression containing 1 equiv. of oxygen ( $O=8$ ), which, in the eyes of those who consider the number 16 as the true molecular value of oxygen, must appear perfectly inadmissible.

IV. "On the Behaviour of the Aldehydes with Acids." By A. GEUTHER, Esq., and R. CARTMELL, Esq. Communicated by Dr. FRANKLAND. Received June 8th, 1859.

[Abstract.]

The authors of this paper, with a view of obtaining a series of combinations homologous with those already obtained from glycol by

Wurz—viz. diacetate of glycol,  $\left. \begin{array}{l} C_4 H_4 \\ C_4 H_3 O_2 \\ C_4 H_3 O_2 \end{array} \right\} O_4$ , and the isomeric body

of Geuther from common aldehyde, by the action of anhydrous acetic acid,—have subjected common aldehyde, acrolein, and oil of bitter almonds to the action of hydrochloric, hydriodic, and sulphurous acids.

#### I. *Acrolein*,—*Metacrolein*.

##### 1. *Acrolein and Hydrochloric Acid*.

By acting on acrolein,  $C_6 H_4 O_2$ , with dry hydrochloric acid gas, a body is formed of the composition  $C_6 H_5 O_2 Cl$ , resulting from a direct combination of one atom of aldehyde with one atom of the acid. This substance is insoluble in water, and can be washed with it in order to free it from any excess of acid or acrolein which may be still present. By drying, which can only be done over sulphuric acid at low temperatures, the body, for which the authors propose the name of hydrochlorate of acrolein, is obtained in a mass of white crystals, presenting a texture like that of velvet. It melts at  $32^\circ C.$  into a thick oil, having a smell of slightly rancid fat. It is

readily soluble in alcohol or ether, on evaporation of which it remains behind as a thick oil. When boiled with water, it remains, as far as can be seen, unchanged. Dilute solutions of the alkalies appear not to act on it. Heated with solution of ammonia, in a sealed tube, at  $100^{\circ}\text{C}$ ., it is decomposed, chloride of ammonium and acrolein ammonia being the result. It does not combine with bichloride of platinum when in solution in alcohol, and very slowly reduces boiling ammoniacal solution of nitrate of silver. Heated alone, it decomposes into acrolein and hydrochloric acid. By the action of concentrated hydrochloric acid acrolein is set free. Dilute sulphuric and nitric acids decompose it likewise, setting acrolein free. Heated with hydrate of potash it gives off hydrogen, and there distils at the same time an oily body, which solidifies into magnificent colourless crystals, analyses of which prove it to be an isomeric acrolein, for which the authors propose the name *Metacrolein*.

Metacrolein as thus obtained is insoluble in water, but is capable of being recrystallized from alcohol or ether. The crystals form very long needles, more especially when melted metacrolein before solidifying is allowed to flow about in a glass tube. They resemble very much in appearance the crystals of acetamide, possess a peculiar aromatic smell, and have a taste at first producing a cooling and afterwards a burning sensation. They are lighter than water. They melt at about  $50^{\circ}\text{C}$ ., becoming solid at about  $45^{\circ}\text{C}$ . Before melting they are somewhat volatilizable, on which account they can be distilled in the vapour of water. On being heated, metacrolein is changed into common acrolein. Dilute alkalies do not effect any change in this substance. By heating with mineral acids, common acrolein is set free. On leading dry hydrochloric acid gas over metacrolein in a bulb-tube, the metacrolein melts and combines with the acid, producing the already-named hydrochlorate of acrolein. From this behaviour, the authors believe the acrolein contained in the combination of hydrochloric acid to be metacrolein, and not common acrolein. If metacrolein be viewed as  $\text{C}_{12}\text{H}_8\text{O}_4$ , the formula of the hydrochloric acid compound would then be  $\text{C}_{12}\text{H}_8\text{O}_4, 2\text{HCl}$ ; and the formation of metacrolein may be assumed to take place according to the following equation,  $\text{C}_{12}\text{H}_8\text{O}_4, 2\text{HCl} + 2\text{KOH} = \text{C}_{12}\text{H}_8\text{O}_4 + 2\text{KCl} + 4\text{HO}$ . The evolution of hydrogen has been found to be the result of a secondary action.

### 2. *Acrolein and Hydriodic Acid.*

These substances act very violently on each other if the acid in the gaseous form be led into acrolein, producing a hissing noise, as when red-hot iron is plunged into water. The resulting substance is insoluble in alcohol, ether, acids, and alkalies. Bisulphide of carbon dissolves out a little free iodine. Heated alone, iodine is set free.

### 3. *Acrolein and Water.*

Acrolein mixed with two or three times its volume of water, and exposed to the temperature of boiling water for eight days, undergoes a gradual change. Acrylic acid is produced, and a resinous substance, soluble in ether, melting at about  $60^{\circ}$ , and becoming solid at  $55^{\circ}\text{C}$ . At common temperatures it is hard and brittle, like resin. The per-centage composition of this resin, on analysis, was found to be the same as that obtained by Redtenbacher, and named Desacrylharz\*, viz. carbon 66.6, hydrogen 7.4.

### 4. *Metacrolein and Hydriodic Acid.*

When dry hydriodic acid gas is passed over dry metacrolein, the latter melts, and changes into a heavy yellow solution, resembling in smell and appearance the hydrochlorate of acrolein. It can be washed with water, and appears at ordinary temperatures to solidify into crystals; placed over sulphuric acid to dry, it decomposes, becoming brown, and setting iodine free. From the analogy in its formation, this compound can be properly viewed as hydriodate of acrolein.

## II. *Aldehyde.*

### 1. *Aldehyde and Hydrochloric Acid.*

Lieben found that by the action of hydrochloric acid on aldehyde, a body of the composition  $\text{C}_8\text{H}_8\text{O}_2\text{Cl}_2$  was produced, having a constant boiling-point of from  $116^{\circ}$  to  $117^{\circ}\text{C}$ .†

The authors confirm Lieben's paper as to the replacement of  $\text{O}_2$  by  $\text{Cl}_2$  in two atoms of aldehyde, and have further obtained a new combination, analysis of it giving the formula as  $\text{C}_{12}\text{H}_{12}\text{O}_4\text{Cl}_2$ , in which two equivalents of oxygen are replaced by the same number of equivalents of chlorine in three atoms of aldehyde. By the action of

\* Liebig's Annalen, vol. xlvii. p. 145.

† Ibid. vol. cvi. p. 336.

water, this compound, like that of Lieben, is resolved into hydrochloric acid and aldehyde. By heat, it is broken up into aldehyde and the body  $C_8H_8O_2Cl_2$ . The authors propose for it the name protoxychloride of aldehyde.

## 2. *Aldehyde and Hydriodic Acid.*

By the action of hydriodic acid on aldehyde a compound is produced that decomposes with water into the aldehyde and the acid again, on which account it could not be purified. On heating, it is suddenly decomposed at  $70^\circ C.$ , leaving a black resinous residue, which on distillation gave off vapours of iodine. In its mode of formation it is analogous to the bodies produced by the action of hydrochloric acid on aldehyde.

## 3. *Aldehyde and Sulphurous Acid—Elaldehyde.*

Dry sulphurous acid gas led into anhydrous aldehyde in cold water is absorbed with great avidity, 11 grammes of aldehyde absorbing 19 grammes of the acid, whilst an increase of volume takes place. The absorption-coefficient of aldehyde for this acid was found to be 1.4 times greater than that of alcohol for the same, and seven times greater than that of water for it. No chemical combination appears to take place, as, on passing a stream of carbonic acid through the fluid at a slightly elevated temperature, almost all the sulphurous acid can be driven out again. If aldehyde, saturated with sulphurous acid, be left for about a week at ordinary temperatures in a well-stoppered bottle, it suffers in this time almost a complete change into a body for which the authors propose at present the name Elaldehyde. To obtain it pure, the fluid is mixed with as much water as is necessary to dissolve it up; the acid is saturated by degrees with chalk, and the fluid obtained is distilled so long as oily drops pass into the receiver. The common aldehyde is separated in a resinous form by digesting for some time with solution of caustic soda or potash. By repeated distillation, the elaldehyde can be obtained free from everything but a little water. Analysis gives the formula of this aldehyde as  $C_4H_4O_2$ . It is therefore isomeric with common aldehyde. As it was obtained in quantity by the foregoing method, its properties were further examined. Its boiling-point was found to be  $124^\circ C.$ , and solidifying-point  $10^\circ C.$  Whilst solidifying it likewise starts

into crystals, the melting-point of which is also  $10^{\circ}\text{C}$ . The aldehyde here described under the name Elaldehyde is identical with that of Weidenbush\*. Its mode of production from common aldehyde is the same; its boiling-point likewise agrees with that of the aldehyde of Weidenbush.

The elaldehyde of Fehling† the authors believe to be identical with that they have obtained, and also that obtained by Weidenbush. That which goes far to prove the identity of the two latter is their vapour-densities. That of Weidenbush's is given as 4.58, whilst that of Fehling's is 4.52; both are converted into common aldehyde by heating gently with dilute sulphuric acid, and both crystallize at low temperatures. The only material discrepancy between them is the boiling-point of  $94^{\circ}\text{C}$ . given by Fehling for elaldehyde, whilst Weidenbush gives the boiling-point of his aldehyde as  $125^{\circ}\text{C}$ .

### III. *Oil of Bitter Almonds.*

#### 1. *Oil of Bitter Almonds and Hydrochloric Acid.*

This acid does not combine with oil of bitter almonds. Experiments made in sealed tubes, heated first to  $100^{\circ}\text{C}$ ., and afterwards to  $200^{\circ}$ , gave no signs of a combination having been effected.

#### 2. *Oil of Bitter Almonds and Hydriodic Acid.*

Much better results can be obtained when hydriodic acid is allowed to act on oil of bitter almonds. The gas is absorbed, producing an increase of volume and of temperature, and at the same time a little water. At the end of the operation two layers appear, of a dark-brown colour. The upper one, which is about a sixth part of the quantity of the under one, consists of concentrated hydriodic acid, whilst the under one, a heavy oil, is a compound of iodine and oil of bitter almonds. To obtain the substance in a pure state, it was first washed well with water, to remove excess of the acid; next treated with moderately strong solution of sulphite of soda, to remove any excess of oil; lastly, on washing with water, the salt was removed from it. It can be dried rapidly over sulphuric acid at a temperature not higher than  $20^{\circ}\text{C}$ . A higher temperature produces gradual decomposition. In the preparation of this sub-

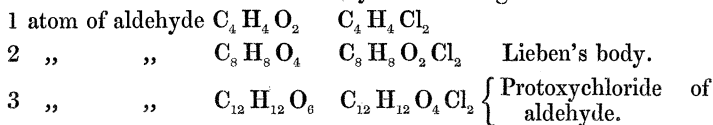
\* Liebig's *Annalen*, vol. lxi. p. 155.

† Liebig's *Annalen*, vol. xxvii. p. 320.

stance, 6 grammes of oil of bitter almonds absorbed 11 grammes of hydriodic acid gas. Analyses of the substance lead to the formula  $C_{42}H_{18}O_2I_4$ , which will be observed to be 3 atoms of oil of bitter almonds, in which  $2(O_2)$  is replaced by  $2(I_2)$ . The authors propose for it the name Oxyiodide of Benzaldehyde. The substance thus obtained melts at  $28^\circ C.$ , and solidifies at about  $25^\circ C.$  into almost colourless rhombic plates if rapidly cooled down. When in a liquid state, the crystals mostly occur in groups of long needles. The colour of the substance in a melted state is brownish yellow; at moderate temperatures, and on standing in the air, it becomes still darker in colour. It possesses a smell very much resembling cress. It volatilizes at common temperatures, its vapour attacking the eyes powerfully. Its vapour at higher temperatures, when carried away by that of water, becomes more and more intolerable, producing a very inflammatory effect on the eyes and nose, which is more painful and permanent than that from acrolein. It is insoluble and sinks in water, but can be distilled in the vapour of it. Watery solutions of carbonates and sulphites of the alkalies do not act on it. Alcoholic solution of potash decomposes it by degrees on heating a little, producing much iodide of potassium, some benzoic acid, and an oily body that remains dissolved in the alcohol, which is not oil of bitter almonds. Alcoholic and watery solutions of ammonia change it slowly into iodide of ammonium and oil of bitter almonds. Boiled with solution of nitrate of silver, it yields iodide of silver, and a smell of oil of bitter almonds. Concentrated hydrochloric acid changes it by degrees, becoming brown; concentrated sulphuric acid dissolves it on heating, with the separation of iodine.

In conclusion, the authors remark that the action of hydrochloric acid on aldehyde may be regarded as consisting in the replacement of two equivalents of oxygen by two of chlorine in one, two, or three atoms of this body: thus,

Aldehyde containing chlorine.



The action of hydriodic acid on oil of bitter almonds gives rise also

to a body derived from 3 atoms of this aldehyde, in which 2 (O<sub>2</sub>) is replaced by 2 (I<sub>2</sub>).

3 atoms of oil of bitter almonds,      Oxyiodide of Benzaldehyde,  
 $C_{42}H_{18}O_6$                                        $C_{42}H_{18}O_2I_4$ .

In the case of acrolein, the action of hydrochloric acid is different ; it combines directly with it, no elimination of water taking place. If we conceive, however, that, in the action of this acid on common aldehyde, the water which is there produced is the effect of a further decomposition, then we may readily suppose that, if this further decomposition had taken place in the case of hydrochloric acid and acrolein, a body derived from two atoms of acrolein, and having O<sub>2</sub> replaced by Cl<sub>2</sub>, corresponding to the second term in the combination of aldehyde and chlorine, would have been the result ; thus—

2 atoms of hydrochlorate of acrolein—

$C_{12}H_{10}O_4Cl_2 - 2(HO) = C_{12}H_8O_2Cl_2$ , corresponding to the  
term  $C_8H_8O_2Cl_2$  in common aldehyde.

There is a curious connexion which may be mentioned, in this substitution of chlorine for oxygen in aldehyde, between the formula of these bodies containing chlorine, and those of the isomeric modifications of aldehyde.

V. "On the Action of Acids on Glycol" (Second Notice.) By  
Dr. MAXWELL SIMPSON. Communicated by Dr. FRANK-  
LAND. Received June 29, 1859.

Since my last communication to the Society, I have discovered a more convenient process for the preparation of chloracetine of glycol. I have ascertained that the monoacetate of glycol is as readily converted into this substance by the action of hydrochloric acid, as a mixture of acetic acid and glycol. As the monoacetate is easily obtained, and for this purpose need not be quite pure, it is possible by this method to prepare the body in question on a large scale and with great facility. It is simply necessary to conduct a stream of dry hydrochloric acid gas into the monoacetate, maintained at the temperature of 100° C., till the quantity of oil precipitated on the